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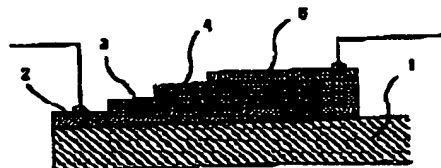


JAPANESE PATENT OFFICE

## PATENT ABSTRACTS OF JAPAN

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**H01L 31/04**(21) Application number: **04059993**(22) Date of filing: **13.03.92**(71) Applicant: **NISSHA PRINTING CO LTD**(72) Inventor:  
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**KITANO HISAO****(54) ORGANIC RECTIFYING ELEMENT****(57) Abstract:****PURPOSE:** To provide an organic rectifying element with excellent rectifying function.**CONSTITUTION:** A glass board 1 is provided with a gold electrode 2 thereon through a sputtering method, etc., and a poly-3-methylthiophene layer is piled up thereon through electrolytic oxidation polymerization. Then it is electrochemically applied with a dedoping treatment to form a high molecular conductive layer 3, a 6-methyl-10-(p-methylbenzyl)-5,10-dihydrophenazine film 4 is deposited on the layer 3 through a vacuum deposition method, and further aluminum 10 vacuum-deposited on the film 4 to form an electrode 5, and thereby an organic rectifying element is realized finally.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The organic rectifying device characterized by carrying out the laminating of 5-(electron releasing group) permutation-10-(aralkyl or nuclear substitution aralkyl)-5, the 10-dihydrophenazine film, a macromolecule conductor ingredient layer, or the metal system ingredient layer.

[Claim 2] The organic rectifying device according to claim 1 which is the layer which a macromolecule conductor ingredient layer turns into from at least one macromolecule conductor ingredient chosen from the group which consists of an organic synthesis system ingredient, an organic pyrolysis system ingredient, and a carbon system ingredient.

[Claim 3] The organic rectifying device according to claim 1 which is the layer which a metal system ingredient layer turns into from at least one metal system ingredient chosen from the group which consists of a metal, an alloy, a metallic oxide, metallic sulfide, and an alloy oxide.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] Generally the organic rectifying device of this invention is widely applicable about an organic rectifying device with new this invention in the industry to which electronics or optoelectronics relates as an electric rectifier, a transistor, the diode for rectification, a photodiode, a light emitting diode, or a switch.

[0002]

[Description of the Prior Art] The Schottky barrier mold component which combined p-mold organic semiconductor and the small metal thin film of a work function as an organic rectifying device is known, and aluminum / metal free phthalocyanine / combination of Au, and aluminum / Poly 3-methylthiophene / combination of Au is studied. Although this invention persons developed the organic bilayer mold optoelectric transducer and clarified the result as JP.59-28388.A and JP.3-91269.A were already shown, they were approached by the need for development of a still more effective organic rectifying device.

[0003]

[Problem(s) to be Solved by the Invention] Although this invention persons present the rectification which is the fault of a Prior art, they look for the organic compound which reinforces rectification efficiently certainly paying attention to the point that it is low effectiveness, they repeat examination about the structure, and, subsequently came to complete composition and its property, and this invention that research is developed and should \*\* carry out it at last this time also about application.

[0004]

[Means for Solving the Problem] this invention persons - it was shown clearly that it has the organic rectification excellent in the component which has the component to which the laminating of 5-(electron releasing group) permutation-10-(aralkyl or nuclear substitution aralkyl)-5, the 10-dihydrophenazine film (it is hereafter called the phenazine film for short), a macromolecule conductor ingredient layer, or the metal system ingredient layer is carried out. The macromolecule conductor ingredient layer said here is a layer which consists of at least one macromolecule conductor ingredient chosen from the group which consists of an organic synthesis system ingredient, an organic pyrolysis system ingredient, and a carbon system ingredient, and a metal system ingredient layer is a layer which consists of at least one metal system ingredient chosen from the group which consists of a metal, an alloy, a metallic oxide, metallic sulfide, and an alloy oxide.

[0005] The electron releasing group in 5-(electron releasing group) permutation-10-(aralkyl or nuclear substitution aralkyl)-5 and 10-dihydrophenazine (it is hereafter called phenazine for short) An alkyl group, an aralkyl radical, the amino group, an alkylamino radical, a dialkylamino radical, They are the acylamino radical, an alkyl acylamino radical, a pyrrolidinyl radical, a PEPRIJIRU radical, a morpholino radical, etc. as a typical thing They are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, t-butyl, a cyclohexyl radical, a methylamino radical, an acetylamino radical, the aralkyl radical shown in the following.

[0006] With 10-(aralkyl or nuclear substitution aralkyl) radical in phenazine, benzyl, a phenylethyl radical and p-alkyl benzyl (for example, p-methylbenzyl radical -) p-ethyl benzyl, p-alkoxy benzyl (for example, p-methoxybenzyl radical), p-amino benzyl and p-(N-permutation amino) benzyl (for example, p-methylamino benzyl -) p-acetylamino benzyl, p-cyano benzyl, p-nitrobenzyl radical, p-fluoro benzyl, p-fluoro methylbenzyl radical, p-chloro benzyl, p-BUOMO benzyl, p-iodine benzyl, m-dialkyl benzyl (for example, 3, 5-dimethylbenzyl radical), m-dialkoxy benzyl (for example, 3 and 5-dimethoxy benzyl -) m-diamino benzyl, m-JI (N-permutation amino) benzyl, m-screw (trifluoromethyl) benzyl, m-dinitro benzyl, m-difluorobenzyl radical, and o-JIKURO benzyl (for example, 2 and 3-dichloro benzyl -) There are 3, 4-dichloro benzyl, m-dichloro benzyl (for example, 2, 4-dichloro benzyl, 3, 5-dichloro benzyl), m-dibromo benzyl, m-diiodo benzyl, etc. In addition, the carbon atomic number of the alkyl group of the aralkyl radical combined at least with 10- of phenazine is 1-4 pieces, and, as for them, it is needless to say that you may branch also with the straight chain.

[0007] As long as this phenazine is the above-mentioned compound, it may be independent or two or more sorts of mixture is sufficient as it. The spacer powder (plastics powder, silica powder, silicone rubber powder, etc.) as the anti-oxidant of an amount, UV stabilizer-proof, and a thickness control material may be added a little for long-term stabilization when such phenazines are used as the film, and little content of the coloring matter (a coloring agent, charge of fluorescence) may be carried out as check material of membranous thickness.

[0008] Among macromolecule conductor ingredients, as an organic synthesis system ingredient Polypyrrole, a Poly 3-methyl pyrrole, Poly 3, 4-dimethyl pyrrole, The poly thiophene, Poly 3-methylthiophene, Poly 3, 4-dimethylthiophene, Poly p-FENIN, polyacetylene, a Poly p-phenylene sulfide, Poly m-phenylene, Poly p-phenylene oxide, polystyrene, polyacetylene, Polyphenyl acetylene, a polyvinyl carbazole, the poly diacetylene, Conductive rubber and the resin which there are the poly pyridine, Pori (N-methyl pyrrole), poly picoline, etc., and these can use doping either a non-doped object or an object, and contain these can also be used.

[0009] As an organic pyrolysis system ingredient, conductive rubber and the resin which there are synthetic graphite, a conductive carbon fiber, pyrolysis polyimide, pyrolysis polyoxadiazole, pyrolysis polyolefine, a pyrolysis polyamide, a pyrolysis polyacrylonitrile, a pyrolysis polyvinyl chloride, pyrolysis polyvinyl alcohol, a pyrolysis epoxy resin, pyrolysis phenol resin, pyrolysis bridge formation, polystyrene, pyrolysis polyisocyanurate, a pyrolysis polypeptide, etc., and these can use doping either a non-doped object or an object, and contain these can also be used among macromolecule conductor ingredients.

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17.09.04

[0010] As a carbon system ingredient, conductive rubber and the resin which there are graphite, glass carbon, furnace black, KETCHIEN Black, acetylene black, petroleum pitch carbide, coal-tar pitch carbide, etc., and these can use doping either a non-doped object or an object, and contain these can also be used among giant-molecule conductor ingredients.

[0011] as a metal system ingredient -- a metal (for example, gold, silver, platinum, palladium, and nickel --) Aluminum, an indium, magnesium, calcium, silicon, titanium, alloys (for example, a palladium alloy and an aluminum alloy --), such as a zirconium A titanium alloy, a Magnesium alloy, a tin alloy, an indium alloy, a regulus metal, a metallic oxide (for example, an aluminum oxide, indium oxide, and silicon oxide --) What made the lattice defect from oxidation titanium, the tin oxide, a zinc oxide, oxidation copper, antimony oxide, a zirconium dioxide, etc. by the dopant, and gave conductivity. Conductive rubber and the resin which there are metallic sulfide (for example, thiol which made the lattice defect from an iron sulfide, a cobalt sulfide, a nickel sulfide, copper sulfide, etc., and gave conductivity), an alloy oxide (the oxide of the above-mentioned alloy or mixture of the above-mentioned metallic oxide), etc., and contain these can also be used.

[0012] The phenazine film said to this invention is prepared between a macromolecule conductor ingredient layer and a macromolecule conductor ingredient layer or in between a macromolecule conductor ingredient layer and metal system ingredient layers or between a metal system ingredient layer and a metal system ingredient layer. Although one laminating of one of these combination is sufficient as that easiest thing, in order to strengthen effectiveness further, it is desirable to make it the condition of for example, a giant-molecule conductor ingredient layer, the phenazine film, a giant-molecule conductor ingredient layer, the phenazine film, a metal system ingredient layer, etc. at a double layer or multilayer structure. In this case, the macromolecule conductor ingredient layer and the metal system ingredient layer of \*\*\*\* exchange \*\*\*\*\* being carried out are natural.

[0013] Although it will be covered with a film if the above laminated material is further required after usually being prepared on substrates (glass, plastics, a film, a metal sheet, a ceramic plate, plastics cast, etc.) and attaching a suitable electrode section, depending on the object, a laminating may be carried out among substrates. Therefore, the thickness of this laminated material may change to arbitration with the thickness of a substrate, the thickness of a macromolecule conductor ingredient layer, or the thickness of a metal system ingredient layer. However, about the phenazine film, it is good to make it the thickness of 200-5000Å by the monolayer. Therefore, although sum total thickness will increase according to the count of multistory when multistory [ of the phenazine film ] is carried out, it is desirable to take care so that thickness of each film may be made thin for the thickness of each phenazine film within the limits of 200-5000Å and it may become about 200-2000Å. In addition, thickness should warn to become homogeneity to the activity.

[0014] One approach of the degrees is adopted as an approach of making the phenazine film of this invention forming. (1) the approach (3) of painting a vacuum deposition method or the sputtering method (2) solution (the cast method being included), and drying -- the approach phenazine film which lays what was film-ized beforehand (an inflatable flexible bag technique, the pasting-up method, the electrostatic sticking method) may patternize in the form planned according to the object, and may carry out etching clearance and it is not only formed all over a laminating side, but may patternize a garbage selectively.

[0015] A fundamental example of the structure of the organic rectifying device by this invention is explained. As shown in drawing 1, the organic rectifying device is constituted by a substrate 1, the electrode 2 formed on the substrate 1, the giant-molecule conductor layer 3 formed on the electrode 2, the phenazine film 4 formed on the giant-molecule conductor layer 3, and the electrode 5 formed on the phenazine film 4.

[0016] As for the electrode 2 prepared on a substrate 1, it is desirable in laboratory to make it the transparent electrode which covered the whole surface of a substrate 1 substantially. A transparent electrode can be formed on the substrates 1, such as a glass plate, a transparency plastics sheet, or a film, by vapor-depositing gold, silver, aluminum, an indium, indium tin oxide (ITO film), and the tin oxide (Nesa membrane). Moreover, an electrode 5 can be formed by vapor-depositing gold, silver, copper, aluminum, or nickel. In addition, when using especially as a monolayer mold, the macromolecule conductor layer 3 can be omitted.

[0017] Although it changes with classes of electrode 2 formed on a substrate 1, when using aluminum as one electrode, as for the fabrication sequence of an organic rectifying device, it is desirable to make the phenazine film of this invention on an aluminum electrode by approaches, such as a vacuum deposition method, the applying method, the cast method, and a spin coat method, and to carry out the laminating of the macromolecule conductor layer on it first. And what is necessary is just to carry out vacuum deposition of the counter electrodes, such as a golden electrode, on it further if needed.

[0018] In using the substrate which, on the other hand, has the transparent electrode formed by the SUPPATA Ling's method etc., for example, a golden electrode, after carrying out the laminating of the macromolecule conductor layer by an electrolytic oxidation polymerization method etc. on a golden electrode and carrying out undoping processing to an electrical machinery chemistry target, it is convenient on it to carry out the laminating of the phenazine film with vacuum deposition etc. Furthermore, what is necessary is just to carry out vacuum deposition of the electrodes, such as aluminum, if needed.

[0019]

[Function] In the organic rectifying device of this invention, effective rectification is performed, for example in the interface barrier of a giant-molecule conductor layer and the phenazine film. Furthermore, since rectification was performed also in the interface of the phenazine film and a metal system ingredient layer, the component which has the rectification excellent conventionally farther than a well-known organic rectifying device could be built.

[0020] By electrical-potential-difference impression of hard flow, although transport of the charge which crosses impregnation of a charge and both layers by electrical-potential-difference impression of the forward direction according to the electric potential gradient which the barrier of a shot key mold or a heterojunction mold was formed, and was spontaneously formed in the interface of a giant-molecule conductor layer and the phenazine film arises in the organic rectifying device of this invention, in order to oppose an electric potential gradient, a current does not flow but functions as diode. Moreover, by optical exposure, separation of a charge arises in an interface and transport of a charge arises in accordance with an electric potential gradient. Therefore, by covering a load and connecting too hastily externally between the two electrodes of an organic rectifying device, a photocurrent is acquired and it functions also as a photodiode. You can make it function also as light emitting diode using emitting light, in case the charge furthermore poured in by electrical-potential-difference impression of the forward direction recombines with the reverse charge in bulk.

[0021]

[Example] About the organic rectifying device of this invention, although experimented in a large number, the example of

representation extracted from the inside of it explains the manufacture approach and its engine performance. In addition, this invention of it not being what limits only to the following examples and is interpreted is natural, and its thing which do not deviate from the meaning and pneuma of this invention and for which it restricts, and an embodiment can be changed and carried out to arbitration is natural.

[0022] an example 1 -- first, the golden electrode was vapor-deposited by the sputter on the glass substrate, and Polly 3-methylthiophene (it is hereafter called PMeT for short) was produced by the electrolytic oxidation polymerization on it. Subsequently, after carrying out undoping processing of this PMeT film at an electrical machinery chemistry target, the laminating of 5-methyl-10-(p-methylbenzyl)-5 and the 10-dihydrophenazine film (it calls for short Following MMDP) was carried out with the vacuum deposition method. the last -- a It top -- aluminum -- vacuum deposition -- carrying out -- Au/PMeT/MMDP/aluminum -- the sandwiches cel of structure was manufactured.

[0023] It impressed changing direct-current applied voltage to this sandwiches cel continuously under dark, and the current-voltage curve was investigated. Drawing 2 and drawing 3 are graphs which show the current change at the time of changing direct-current applied voltage continuously. Consequently, it was checked that the stable rectification from which the time of impressing a forward electrical potential difference to a golden electrode side serves as the forward direction occurs. The current value when the current value when impressing the electrical potential difference of +4V to a golden electrode impresses the electrical potential difference of +14.0mA and -4V was the rectification ratio 120000 in -0.117microA (refer to drawing 2). Moreover, in the applied voltage of \*\*2V, it was the rectification ratio 18000 in the current value of +1.05mA and -0.058microA, respectively (refer to drawing 3).

[0024] Next, when light was irradiated at this component, the golden electrode side produced photoelectromotive force in the direction used as forward. At this time, change of the photocurrent at the time of changing the wavelength of light to irradiate was measured. Drawing 4 is the graph of the action spectrum in which the relation of a light wave length-photocurrent is shown. From this graph, when an optical exposure is carried out from a golden electrode side, since [ of the absorption maximum of (-) and PMeT ] a photocurrent value serves as the minimum by the way, the screen effect by PMeT is shown, and it turns out that an activity side is not the interface of a golden electrode and a PMeT layer but the back of a PMeT layer. Moreover, since a photocurrent value serves as the maximum (O) and near the skirt of absorption of MMDP when an optical exposure is carried out from an aluminum electrode side, the screen effect by MMDP is shown, and it turns out that a main activity side is the back of a MMDP layer, i.e., the interface of PMeT and MMDP. In addition, since the monolayer mold component which sandwiched only MMDP with a golden electrode and aluminum carries out rectification and a photo-electric-translation operation in a bilayer mold component and this direction, the interface of aluminum and MMDP is also known by functioning as an activity side.

[0025] In example 2 example 1 instead of MMDP 5-methyl-10-(p-methoxybenzyl)-5, 10-dihydrophenazine 5-methyl-(hereafter called MMDP for short) 10-(p-cyano benzyl)-5, 10-dihydrophenazine The same sandwiches cel was manufactured using (it being hereafter called MCDP for short) or 5-methyl-10-(m-dinitro benzyl)-5, and 10-dihydrophenazine (it is hereafter called MDNDP for short). When impressed changing direct-current applied voltage to these sandwiches cels continuously under dark, a current change similar to drawing 2 was shown, and it was checked that the same rectification occurs. A rectification ratio is the component which used MMDP, and is 1200 (\*\*4v) with 10000 (\*\*4v) and the component using MDNDP in the component using 12000 (\*\*2v) and MCDP, and it turned out that it has the rectification which was excellent in all.

[0026] In example 3 example 1, rectification remarkable also in \*\*\*\* which used other macromolecule conductor ingredient layers was accepted instead of the PMeT layer. The name and rectification ratio (\*\*2V) of the layer ingredient were as follows. That is, they are polypyrrole (rectification ratio 16000), Polly 3, 4-dimethyl pyrrole (rectification ratio 18000), Pori p-phenylene (rectification ratio 13000), the poly thiophene (rectification ratio 1200), polyacetylene (rectification ratio 1000), polish anoa cetylene (rectification ratio 2000), a polyvinyl carbazole (rectification ratio 1000), pyrolysis polyimide (rectification ratio 8000), a pyrolysis polyacrylonitrile (rectification ratio 5000), and graphite (rectification ratio 6000). Moreover, when a metal system ingredient was used similarly, the result of an indium (rectification ratio 12000), aluminum magnesium (rectification ratio 15000), a zinc chloride doping aluminum oxide (rectification ratio 4000), antimony-pentachloride doping tin oxide (rectification ratio 14000), and conductive copper sulfide (rectification ratio 10000) was obtained.

[0027] [Effect of the Invention] Since the organic rectifying device of this invention rectified efficiently using both interface barriers of for example, the interface barrier of a giant-molecule conductor ingredient layer and the phenazine film, the phenazine film, and a metal system ingredient layer, it became possible [ making the component which gives the rectification ratio excellent conventionally farther than a well-known organic rectifying device ]. Moreover, since the electron and electron hole which photocharge separation was performed using this barrier, consequently were separated are mutually conveyed to an opposite direction, it functions also as an optoelectric transducer. Furthermore, while the charge poured in by electrical-potential-difference impression moves in accordance with the electric potential gradient of a barrier in the inside of bulk, it functions also as electroluminescence devices using recombining with a reverse charge and emitting light. Therefore, it is sure that the predominance of the application in the industrial world of this invention is a greatest object.

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## TECHNICAL FIELD

[Industrial Application] Generally the organic rectifying device of this invention is widely applicable about an organic rectifying device with new this invention in the industry to which electronics or optoelectronics relates as an electric rectifier, a transistor, the diode for rectification, a photodiode, a light emitting diode, or a switch.

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**PRIOR ART**

[Description of the Prior Art] The Schottky barrier mold component which combined p-mold organic semiconductor and the small metal thin film of a work function as an organic rectifying device is known, and aluminum / metal free phthalocyanine / combination of Au, and aluminum / Poly 3-methylthiophene / combination of Au is studied. Although this invention persons developed the organic bilayer mold optoelectric transducer and clarified the result as JP,59-28388,A and JP,3-91269,A were already shown, they were approached by the need for development of a still more effective organic rectifying device.

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**EFFECT OF THE INVENTION**

[Effect of the Invention] Since the organic rectifying device of this invention rectified efficiently using both interface barriers of for example, the interface barrier of a giant-molecule conductor ingredient layer and the phenazine film, the phenazine film, and a metal system ingredient layer, it became possible [ making the component which gives the rectification ratio excellent conventionally farther than a well-known organic rectifying device ]. Moreover, since the electron and electron hole which photocharge separation was performed using this barrier, consequently were separated are mutually conveyed to an opposite direction, it functions also as an optoelectric transducer. Furthermore, while the charge poured in by electrical-potential-difference impression moves in accordance with the electric potential gradient of a barrier in the inside of bulk, it functions also as electroluminescence devices using recombining with a reverse charge and emitting light. Therefore, it is sure that the predominance of the application in the industrial world of this invention is a greatest object.

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## MEANS

[Means for Solving the Problem] this invention persons — It was shown clearly that it has the organic rectification excellent in the component which has the component to which the laminating of 5-(electron releasing group) permutation-10-(aralkyl or nuclear substitution aralkyl)-5, the 10-dihydrophenazine film (it is hereafter called the phenazine film for short), a macromolecule conductor ingredient layer, or the metal system ingredient layer is carried out. The macromolecule conductor ingredient layer said here is a layer which consists of at least one macromolecule conductor ingredient chosen from the group which consists of an organic synthesis system ingredient, an organic pyrolysis system ingredient, and a carbon system ingredient, and a metal system ingredient layer is a layer which consists of at least one metal system ingredient chosen from the group which consists of a metal, an alloy, a metallic oxide, metallic sulfide, and an alloy oxide.

[0005] The electron releasing group in 5-(electron releasing group) permutation-10-(aralkyl or nuclear substitution aralkyl)-5 and 10-dihydrophenazine (it is hereafter called phenazine for short) An alkyl group, an aralkyl radical, the amino group, an alkylamino radical, a dialkylamino radical, They are the acylamino radical, an alkyl acylamino radical, a pyrrolidiny radical, a PEPRIJIRU radical, a morpholino radical, etc. as a typical thing They are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, t-butyl, a cyclohexyl radical, a methylamino radical, an acetylamino radical, the aralkyl radical shown in the following.

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[0009] As an organic pyrolysis system ingredient, conductive rubber and the resin which there are synthetic graphite, a conductive carbon fiber, pyrolysis polyimide, pyrolysis polyoxadiazole, pyrolysis polyolefine, a pyrolysis polyamide, a pyrolysis polyacrylonitrile, a pyrolysis polyvinyl chloride, pyrolysis polyvinyl alcohol, a pyrolysis epoxy resin, pyrolysis phenol resin, pyrolysis bridge formation polystyrene, pyrolysis polyisocyanurate, a pyrolysis polypeptide, etc., and these can use doping either a non-doped object or an object, and contain these can also be used among macromolecule conductor ingredients.

[0010] As a carbon system ingredient, conductive rubber and the resin which there are graphite, glass carbon, furnace black, KETCHIEN black, acetylene black, petroleum pitch carbide, coal-tar pitch carbide, etc., and these can use doping either a non-doped object or an object, and contain these can also be used among giant-molecule conductor ingredients.

[0011] as a metal system ingredient — a metal (for example, gold, silver, platinum, palladium, and nickel —) Aluminum, an indium, magnesium, calcium, silicon, titanium, alloys (for example, a palladium alloy and an aluminum alloy —), such as a zirconium / titanium alloy, a Magnesium alloy, a tin alloy, an indium alloy, a regulus metal, a metallic oxide (for example, an aluminum oxide, indium oxide, and silicon oxide —) What made the lattice defect from oxidization titanium, the tin oxide, a zinc oxide, oxidization copper, antimony oxide, a zirconium dioxide, etc. by the dopant, and gave conductivity, Conductive rubber and the resin which there are metallic sulfide (for example, thing which made the lattice defect from an iron sulfide, a cobalt sulfide, a nickel sulfide, copper sulfide, etc., and gave conductivity), an alloy oxide (the oxide of the above-mentioned alloy or mixture of the above-mentioned metallic oxide), etc., and contain these can also be used.

[0012] The phenazine film said to this invention is prepared between a macromolecule conductor ingredient layer and a macromolecule conductor ingredient layer or in between a macromolecule conductor ingredient layer and metal system ingredient layers or between a metal system ingredient layer and a metal system ingredient layer. Although one laminating of one of these combination is sufficient as that easiest thing, in order to strengthen effectiveness further, it is desirable to make it the condition of for example, a giant-molecule conductor ingredient layer, the phenazine film, a giant-molecule conductor ingredient layer, the phenazine film, a metal system ingredient layer, etc. at a double layer or multilayer structure. In this case, the macromolecule conductor ingredient layer and the metal

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system ingredient layer of \*\*\*\* exchange \*\*\*\*\* being carried out are natural.

[0013] Although it will be covered with a film if the above laminated material is further required after usually being prepared on substrates (glass, plastics, a film, a metal sheet, a ceramic plate, plastics cast, etc.) and attaching a suitable electrode section, depending on the object, a laminating may be carried out among substrates. Therefore, the thickness of this laminated material may change to arbitration with the thickness of a substrate, the thickness of a macromolecule conductor ingredient layer, or the thickness of a metal system ingredient layer. However, about the phenazine film, it is good to make it the thickness of 200-5000Å by the monolayer. Therefore, although sum total thickness will increase according to the count of multistory when multistory [ of the phenazine film ] is carried out, it is desirable to take care so that thickness of each film may be made thin for the thickness of each phenazine film within the limits of 200-5000Å and it may become about 200-2000Å. In addition, thickness should warn to become homogeneity to the activity.

[0014] One approach of the degrees is adopted as an approach of making the phenazine film of this invention forming.

(1) the approach (3) of painting a vacuum deposition method or the sputtering method (2) solution (the cast method being included), and drying -- the approach phenazine film which lays what was film-ized beforehand (an inflatable flexible bag technique, the pasting-up method, the electrostatic sticking method) may patternize in the form planned according to the object, and may carry out etching clearance and it is not only formed all over a laminating side, but may patternize a garbage selectively.

[0015] A fundamental example of the structure of the organic rectifying device by this invention is explained. As shown in drawing 1, the organic rectifying device is constituted by a substrate 1, the electrode 2 formed on the substrate 1, the giant-molecule conductor layer 3 formed on the electrode 2, the phenazine film 4 formed on the giant-molecule conductor layer 3, and the electrode 5 formed on the phenazine film 4.

[0016] As for the electrode 2 prepared on a substrate 1, it is desirable in laboratory to make it the transparent electrode which covered the whole surface of a substrate 1 substantially. A transparent electrode can be formed on the substrates 1, such as a glass plate, a transparency plastics sheet, or a film, by vapor-depositing gold, silver, aluminum, an indium, indium tin oxide (ITO film), and the tin oxide (Nesa membrane). Moreover, an electrode 5 can be formed by vapor-depositing gold, silver, copper, aluminum, or nickel. In addition, when using especially as a monolayer mold, the macromolecule conductor layer 3 can be omitted.

[0017] Although it changes with classes of electrode 2 formed on a substrate 1, when using aluminum as one electrode, as for the fabrication sequence of an organic rectifying device, it is desirable to make the phenazine film of this invention on an aluminum electrode by approaches, such as a vacuum deposition method, the applying method, the cast method, and a spin coat method, and to carry out the laminating of the macromolecule conductor layer on it first. And what is necessary is just to carry out vacuum deposition of the counter electrodes, such as a golden electrode, on it further if needed.

[0018] In using the substrate which, on the other hand, has the transparent electrode formed by the SUPPATA Ling's method etc., for example, a golden electrode, after carrying out the laminating of the macromolecule conductor layer by an electrolytic oxidation polymerization method etc. on a golden electrode and carrying out undoping processing to an electrical machinery chemistry target, it is convenient on it to carry out the laminating of the phenazine film with vacuum deposition etc. Furthermore, what is necessary is just to carry out vacuum deposition of the electrodes, such as aluminum, if needed.

[Translation done.]

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## OPERATION

[Function] In the organic rectifying device of this invention, effective rectification is performed, for example in the interface barrier of a giant-molecule conductor layer and the phenazine film. Furthermore, since rectification was performed also in the interface of the phenazine film and a metal system ingredient layer, the component which has the rectification excellent conventionally farther than a well-known organic rectifying device could be built.

[0020] By electrical-potential-difference impression of hard flow, although transport of the charge which crosses impregnation of a charge and both layers by electrical-potential-difference impression of the forward direction according to the electric potential gradient which the barrier of a shot key mold or a heterojunction mold was formed, and was spontaneously formed in the interface of a giant-molecule conductor layer and the phenazine film arises in the organic rectifying device of this invention, in order to oppose an electric potential gradient, a current does not flow but functions as diode. Moreover, by optical exposure, separation of a charge arises in an interface and transport of a charge arises in accordance with an electric potential gradient. Therefore, by covering a load and connecting too hastily externally between the two electrodes of an organic rectifying device, a photocurrent is acquired and it functions also as a photodiode. You can make it function also as light emitting diode using emitting light, in case the charge furthermore poured in by electrical-potential-difference impression of the forward direction recombines with the reverse charge in bulk.

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## EXAMPLE

[Example] About the organic rectifying device of this invention, although experimented in a large number, the example of representation extracted from the inside of it explains the manufacture approach and its engine performance. In addition, this invention of it not being what limits only to the following examples and is interpreted as natural, and its thing which do not deviate from the meaning and pneumonia of this invention and for which it restricts, and an embodiment can be changed and carried out to arbitration is natural.

[0022] an example 1 - first, the golden electrode was vapor-deposited by the sputter on the glass substrate, and Polly 3-methylthiophene (it is hereafter called PMeT for short) was produced by the electrolytic oxidation polymerization on it. Subsequently, after carrying out undoping processing of this PMeT film at an electrical machinery chemistry target, the laminating of 5-methyl-10-(p-methylbenzyl)-5 and the 10-dihydrophenazine film (it calls for short Following MMDP) was carried out with the vacuum deposition method. the last - a it top - aluminum - vacuum deposition - carrying out - Au/PMeT/MMDP/aluminum - the sandwiches cel of structure was manufactured.

[0023] It impressed changing direct-current applied voltage to this sandwiches cel continuously under dark, and the current-voltage curve was investigated. Drawing 2 and drawing 3 are graphs which show the current change at the time of changing direct-current applied voltage continuously. Consequently, it was checked that the stable rectification from which the time of impressing a forward electrical potential difference to a golden electrode side serves as the forward direction occurs. The current value when the current value when impressing the electrical potential difference of +4V to a golden electrode impresses the electrical potential difference of +14.0mA and -4V was the rectification ratio 120000 in -0.117microA (refer to drawing 2). Moreover, in the applied voltage of \*\*2V, it was the rectification ratio 18000 in the current value of +1.05mA and -0.058microA, respectively (refer to drawing 3).

[0024] Next, when light was irradiated at this component, the golden electrode side produced photoelectromotive force in the direction used as forward. At this time, change of the photocurrent at the time of changing the wavelength of light to irradiate was measured. Drawing 4 is the graph of the action spectrum in which the relation of a light wave length-photocurrent is shown. From this graph, when an optical exposure is carried out from a golden electrode side, since [ of the absorption maximum of (-) and PMeT ] a photocurrent value serves as the minimum by the way, the screen effect by PMeT is shown, and it turns out that an activity side is not the interface of a golden electrode and a PMeT layer but the back of a PMeT layer. Moreover, since a photocurrent value serves as the maximum (O) and near the skirt of absorption of MMDP when an optical exposure is carried out from an aluminum electrode side, the screen effect by MMDP is shown, and it turns out that a main activity side is the back of a MMDP layer, i.e., the interface of PMeT and MMDP. In addition, since the monolayer mold component which sandwiched only MMDP with a golden electrode and aluminum carries out rectification and a photo-electric-translation operation in a bilayer mold component and this direction, the interface of aluminum and MMDP is also known by functioning as an activity side.

[0025] In example 2 example 1 instead of MMDP 5-methyl-10-(p-methoxybenzyl)-5, 10-dihydrophenazine 5-methyl-(hereafter called MMODP for short) 10-(p-cyano benzyl)-5, 10-dihydrophenazine The same sandwiches cel was manufactured using (it being hereafter called MCDP for short) or 5-methyl-10-(m-dinitro benzyl)-5, and 10-dihydrophenazine (it is hereafter called MDNDP for short). When impressed changing direct-current applied voltage to these sandwiches cells continuously under dark, a current change similar to drawing 2 was shown, and it was checked that the same rectification occurs. A rectification ratio is the component which used MMODP, and is 1200 (\*\*4v) with 10000 (\*\*4v) and the component using MDNDP in the component using 12000 (\*\*2v) and MCDP, and it turned out that it has the rectification which was excellent in all.

[0026] In example 3 example 1, rectification remarkable also in \*\*\*\* which used other macromolecule conductor ingredient layers was accepted instead of the PMeT layer. The name and rectification ratio (\*\*2V) of the layer ingredient were as follows. That is, they are polypyrrole (rectification ratio 16000), Polly 3, 4-dimethyl pyrrole (rectification ratio 18000), Pori p-phenylene (rectification ratio 15000), the poly thiophene (rectification ratio 1200), polyacetylene (rectification ratio 1000), polish anoa cetylene (rectification ratio 2000), a polyvinyl carbazole (rectification ratio 1000), pyrolysis polyimide (rectification ratio 8000), a pyrolysis polyacrylonitrile (rectification ratio 5000), and graphite (rectification ratio 6000). Moreover, when a metal system ingredient was used similarly, the result of an indium (rectification ratio 12000), aluminum magnesium (rectification ratio 15000), a zinc chloride doping aluminum oxide (rectification ratio 4000), antimony-pentachloride doping tin oxide (rectification ratio 14000), and conductive copper sulfide (rectification ratio 10000) was obtained.

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## DESCRIPTION OF DRAWINGS

## [Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing one example of the organic rectifying device of this invention.

[Drawing 2] It is the graph which shows the current-voltage characteristic of the organic rectifying device of this invention.

[Drawing 3] It is the graph which shows the current-voltage characteristic of the organic rectifying device of this invention.

[Drawing 4] It is the graph which shows the absorption spectrum of the photocurrent action spectrum of the organic rectifying device of this invention, PMeT, and MMDP.

## [Description of Notations]

1 Substrate

2 Electrode

3 Macromolecule Conductor Layer

4 Phenazine Film

5 Electrode

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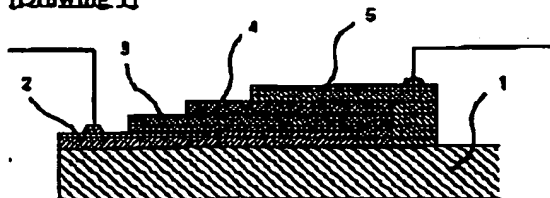
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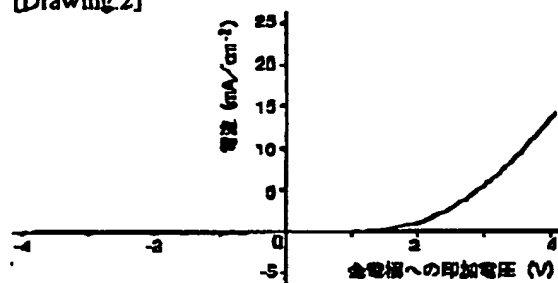
## DRAWINGS

[Drawing 1]

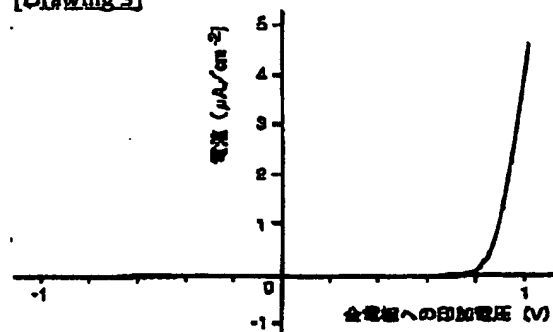


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- 2 電極
- 3 高分子電解質層
- 4 フェナジン膜
- 5 電極

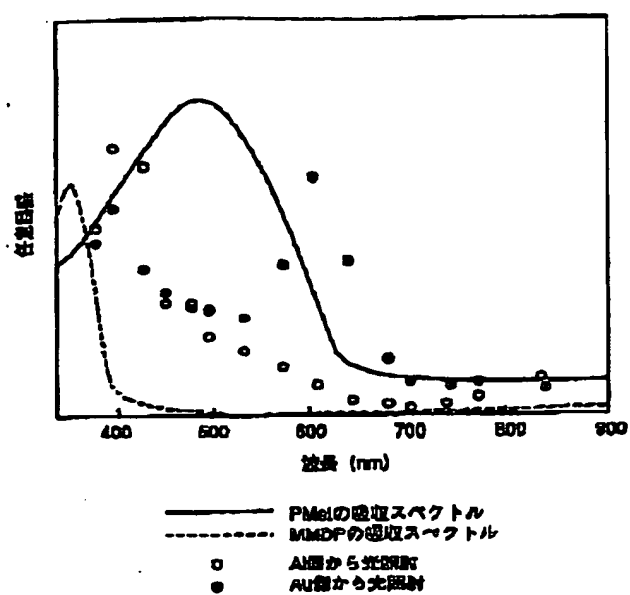
[Drawing 2]



[Drawing 3]

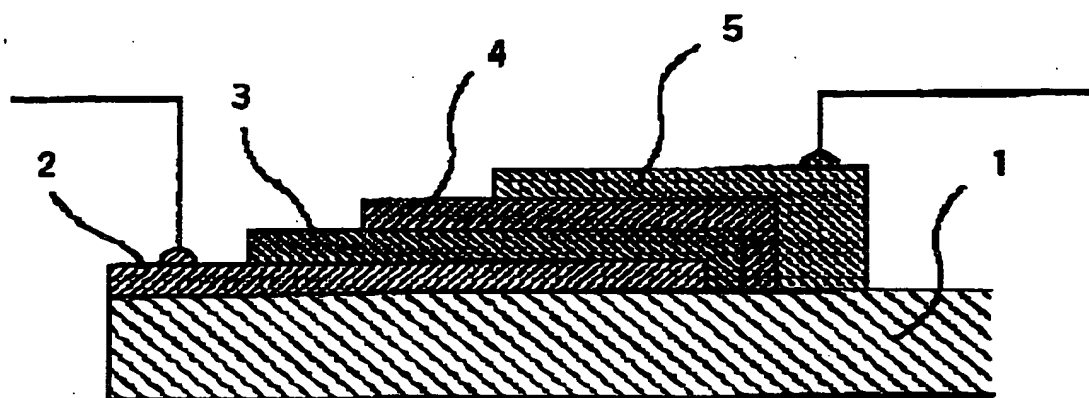


[Drawing 4]



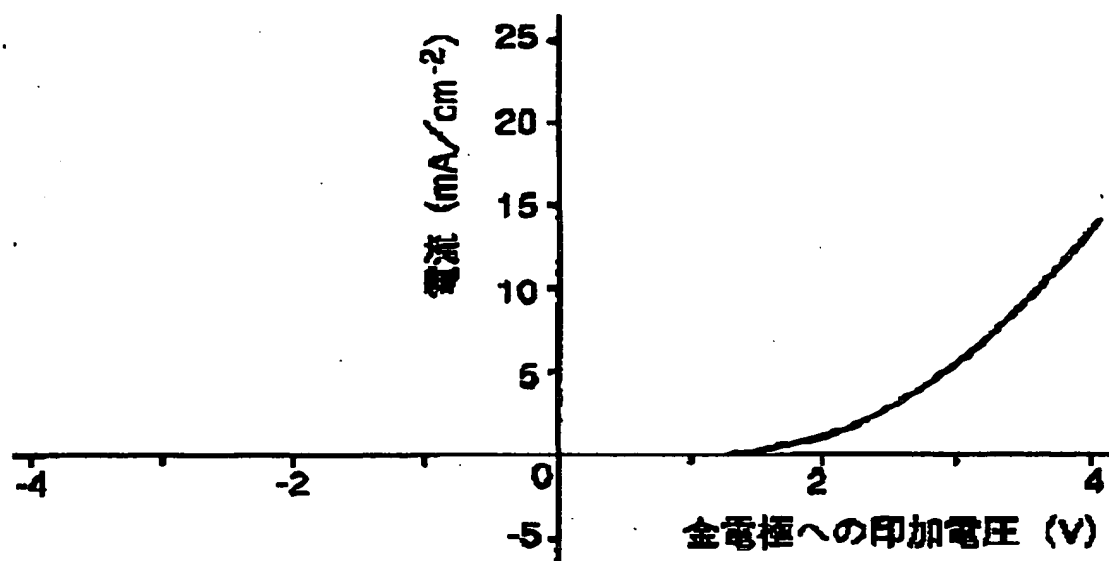
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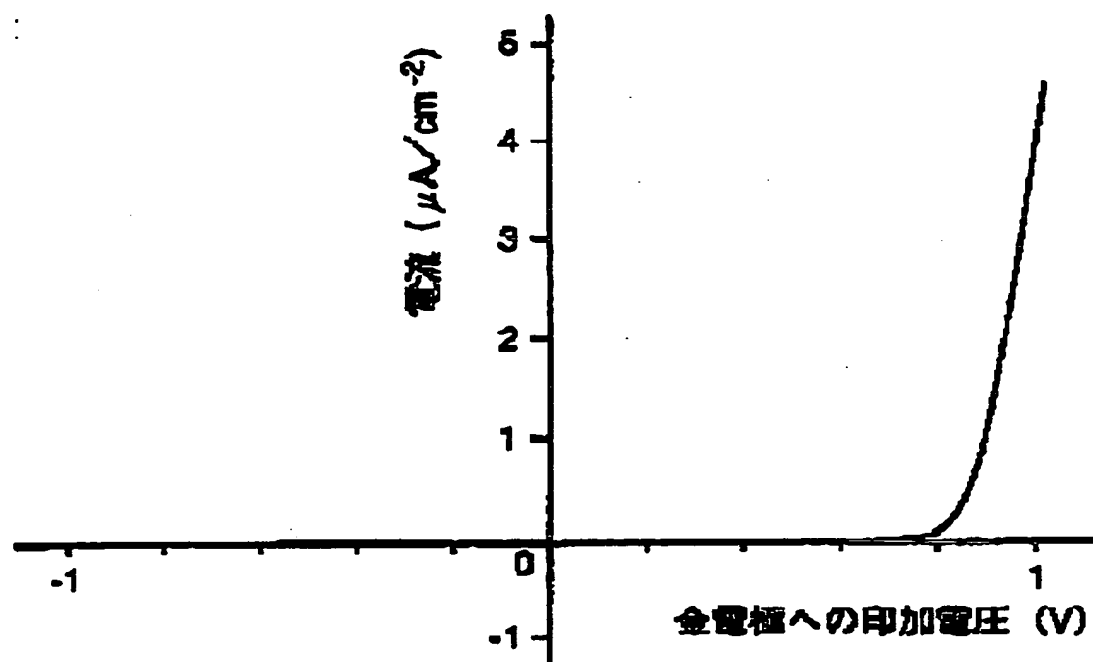


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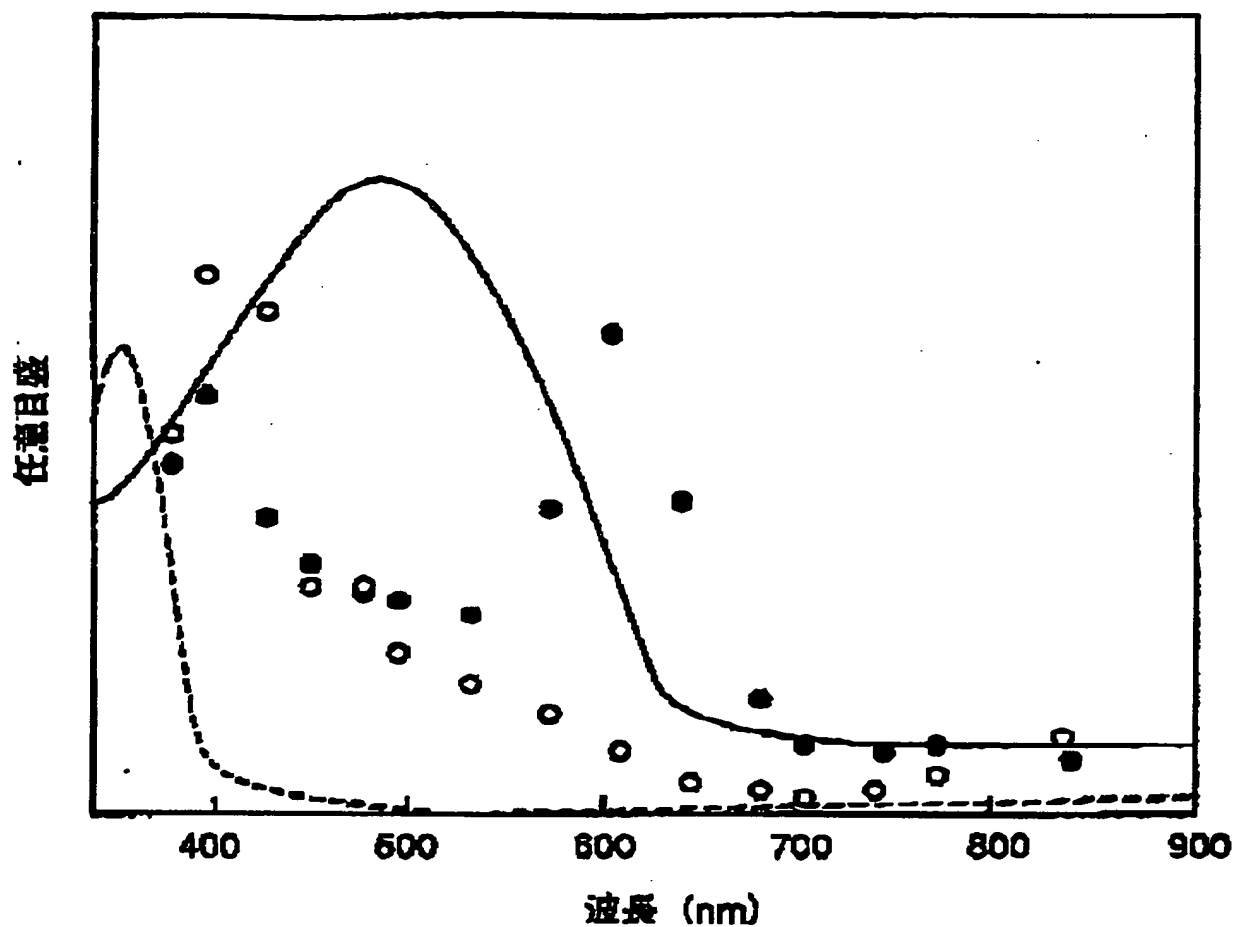
Drawing 1



Drawing 2



Drawing 3



Drawing 4

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